



The role of active species in the N₂ and N₂-H₂ RF afterglows on selective surface nitriding of ALD-grown TiO₂ films



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ABSTRACT

We find that surface modification characteristics of TiO₂ using N₂ RF plasma are strongly dependent on the detailed composition of active species in the plasma and the afterglows. The surface nitriding of ALD-grown TiO₂ films in pure N₂ RF afterglows at room temperature (RT) is found to be more effective in the late afterglows than in the early afterglows. Adding a small fraction of H₂ in N₂ results in suppression of surface nitriding, suggesting that the change in the composition of the active species in the afterglows by H₂ is the origin to the suppressed nitriding performance. Here, we present our analysis on the surface chemical composition after the plasma modification as well as the densities of excited species such as N atoms, N₂(A) and N₂(X, v) metastable molecules and N₂⁺ ions in the afterglows of RF N₂ and N₂-H₂ (<5%) at different positions along the downstream by emission spectroscopy. The early afterglow of N₂ changes from a pink to a late afterglow where the N + N recombination is the dominant process with the introduction of H₂. The roles of active species such as N-atoms and N₂⁺ ions on TiO₂ surface nitriding are found to oppose to each other. We find that N atoms enhance the surface nitriding, while N₂⁺ ions are likely to deplete the surface-bound N species.

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1. Introduction

The fascinating photo-responsive properties of TiO₂ in driving number of photocatalytic reactions [1,2] as well as the huge potential of engineering their electronic structure [3] and morphology [4–6] have led to intense research activities on TiO₂ as can be found from huge publications on TiO₂ in diverse applications such as water splitting [7], sensors [8], solar cells [9] and photocatalytic remediation [3].

The basic principle underlying such diverse applications of TiO₂ is based on the photoexcitation of electrons from valence band (VB) to conduction band (CB) to produce excitons and their subsequent dynamics within the lattice [10,11]. For a high efficiency in photocatalytic or photovoltaic applications, the separation of those excitons, diffusion and reactions at the surface need to be achieved in a favorable way [2, 11]. In this regard, the surface modification of TiO₂ has the utmost influence on the ultimate performance of TiO₂ in such applications since all catalytic reactions take place at the interface between the catalyst and the reactants either in liquid or in gas phases [4,12–14]. The presence of defects or impurities at the surface has a significant influence on

the overall efficiency in photocatalytic [15–17] or photoelectrochemical processes [18].

Among many different surface modification techniques, plasma treatments have been employed many times to turn out to be quite effective in enhancing the photoresponse of TiO₂ materials [12,13,15–19]. In this case, the role of plasma treatments is generally suggested to have a beneficial effect on the enhancement of absorption of visible light [13, 16,19]. However, the influence of plasma treatments on the material's chemical structure can be widely different from the formation of reduced phases (e.g., TiO_{2-x}) [15] with oxygen vacancies [16,17] to the introduction of nitride phases [12,19]. In this regard, the information on the type of active species in plasma responsible for the formation of new structures in the oxide materials would be valuable in engineering the material's property in a more controlled manner.

The promotional effect of plasma treatment on the material's catalytic properties may be further enhanced by optimizing the right condition for the surface treatment. For such a purpose, analysis on the active species in the plasmas and afterglows would provide a valuable information in determining the right condition. With this motivation in mind, we performed a systematic analysis on the active species in the N₂ and N₂-H₂ flowing RF afterglows by emission spectroscopy and the resulting surface nitriding characteristics of TiO₂ films in the afterglows were analyzed by X-ray photoelectron spectroscopy (XPS).

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N_2 and N_2 - H_2 flowing microwave and RF afterglows studied by emission spectroscopy [20–22] are generally understood to have various kinds of active species such as the N atoms, the $N_2(X, v)$ vibrational excited ground state, the $N_2(A, a')$ metastable molecules and the N_2^+ ions, which are determined by the result of complicated kinetic reactions in early and late afterglows [23–25]. The density of N-atoms, O-atoms in impurity, $N_2(X, v > 13)$ and $N_2(A)$ metastable molecules and N_2^+ ions in the afterglows have been quantitatively measured in RF (13.6 MHz) flowing afterglows by NO titration for N atoms and band-ratio intensities for O atoms, $N_2(A)$ and $N_2(X, v > 13)$ metastable molecules and N_2^+ ions. Interesting finding in relation to changes in the active species density in N_2 - H_2 afterglows is that the early afterglow changed from a pink (characterized by a strong emission of N_2^+ ions) to a late afterglow (where the N atoms are dominant without N_2^+ ions) by introducing a small amount (10^{-5} – 10^{-3}) of H_2 into N_2 [21].

In this report, we present our analysis on the densities of N-atoms, O-atoms in impurity, $N_2(X, v > 13)$ and $N_2(A)$ metastable molecules and N_2^+ ions in the N_2 and N_2 - H_2 (<5%) early and late RF afterglows and their influences on the surface nitriding characteristics of the TiO_2 films. Since the treatment condition only allows the chemical changes at the skin-depth layer at the surface, we find a strong correlation between the densities of active species in the afterglows and the surface N content determined by the XPS analysis.

2. Experimental details

The experimental set-up of the RF plasmas and afterglows is reproduced in Fig. 1 [26]. An afterglow quartz tube of 21 mm (I.D.) is connected to a discharge tube of 6 mm (I.D.). The RF plasma is produced between two rings separated by 2 cm in the discharge tube.

Fig. 1(a) shows typical discharge characteristics of RF plasmas of pure N_2 and $N_2 + H_2$ as well as their afterglows. At the operating condition of N_2 flow rate of 1 slm, the pressure of 8 Torr and the applied power of 100 W, one can observe an afterglow starting at around $z = 22$ cm after the capacitive RF discharge between the two Cu strips in the discharge tube. An early afterglow at the beginning extends along the 21 mm dia. Quartz tube up to about 15 cm long downstream and then a late afterglow appears starting at $z = 48$ cm. The plasmas and the afterglows produce characteristic emissions originated from the neutral and ionized excited species of N_2 , which can be measured by the optical emission spectra. The emission spectroscopy is performed by means of an optical fiber connected to a Monera 500 spectrometer

with 500 mm focal length, grating blazed at 500 nm, slits of 0.5 mm, resolution of 0.8 nm and a PMT (Hamamatsu R928 at 900 V).

Fig. 1(a) also shows the picture of N_2 - H_2 RF plasma and its afterglows. Here, we find that the emission intensity in the afterglow region is dramatically reduced compared to that of N_2 afterglow as has been observed earlier [21]; the early (pink) afterglow changes to a late afterglow at $z = 26$ cm with the N_2 - H_2 mixture.

For the evaluation of plasma nitriding characteristics, TiO_2 films were grown on a HF-cleaned Si substrate ((111), p-type, LG Siltron) by atomic-layer deposition (ALD) cycles (250 cycles) of titanium tetrakisopropoxide (TTIP) and H_2O at the substrate temperature of 220 °C and the resulting film thickness is measured to be about 50 nm. The bulk phase of the ALD-grown TiO_2 films is determined to be anatase from X-ray diffraction (XRD) measurements.

For the surface treatment of the TiO_2 films in the afterglows, the sample was introduced into the 21 mm quartz tube at $z = 26$ cm (the pink afterglow of the N_2 RF plasma) and 61 cm (the late afterglow of the N_2 RF plasma), respectively. For the N_2 - H_2 case, the treatment position of 26 cm is selected since the position offers a high density of N atoms ($\sim 10^{15} \text{ cm}^{-3}$) in late afterglow conditions.

The X-ray photoelectron spectroscopy (XPS) measurements were performed in a PHI5000 Versa Probe II (Ulvac-PHI) system using a monochromatic Al K α source. The instrument work function is calibrated to the Au 4f $_{7/2}$ core level binding energy (BE) of 83.96 eV from a metallic gold film. The X-ray beam diameter can be set to 200 μm and a charge neutralizer is used to minimize an undesirable charging effect. The binding energy for the spectra is referred by the C 1s peak from ubiquitous hydrocarbon to 284.8 eV.

3. Results and discussion

3.1. Pure N_2 pink and late afterglows

As shown in Fig. 2 the typical emission spectra of N_2 are characterized by the N_2 first positive (1st pos.) in the red part of spectrum between 500 and 1100 nm and by the N_2 second positive (2nd pos.), N_2^+ first negative (1st neg.) in the UV-blue part between 300 and 400 nm [21,26,27]. The characteristic N_2 emissions are the 1st pos. (580 nm), 2nd pos. (316 nm) and N_2^+ 1st neg. (391.4 nm) bands. The NO_β band at 320 nm is also detected in the N_2 afterglow (Fig. 2(a)) coming from air impurity [27–29]. The NH (336 nm) emission is detected in N_2 - H_2 (2%) as shown in Fig. 2(b).

After calibration of N atom density by NO titration [26], the density of N-atoms, O-atoms in impurity, $N_2(X, v > 13)$ and $N_2(A)$ metastable molecules and N_2^+ ions are obtained by the line-ratio intensity method [27] and the results are reported in Table 1.

The a_{N+N} factor indicates the fraction of N + N recombination in the afterglow: $a_{N+N} = 0$ for pure pink (0%) and $a_{N+N} = 1$ for pure late (100%). Under the present operating condition of Table 1, a_{N+N} is measured to be 12% and 85% at $z = 35$ and 61 cm, respectively.

The N-atom density calibrated by NO titration is obtained with an uncertainty of 30%. Only the order of magnitude of density is expected for the other active species: $N_2(X, v > 13)$, $N_2(A)$ and N_2^+ which are depending on kinetic rates of the chosen dominant reactions.

To interpret the results in Table 1, it must be considered that the radial distribution of radiative states is sharp in the pink afterglow as reported in [21] at 8 Torr, 1 slm, 100 W, $z = 32$ cm. The half-intensity width of the late afterglow is twice larger than that of the pink afterglow; that is, the pink afterglow has a narrower radial distribution in the tube than the late afterglow by a factor of a half. However, the estimated densities of active species from the emission data give only average values across the diameter of the tube since the emission intensity is the integrated emission along the line-of-sight. Thus, the densities at the center should be higher by a factor of two if the half-intensity width becomes narrower by half. Thus, the excited species densities in the pink afterglow reported in Table 1 at $z = 35$ cm are multiplied by 2 to be

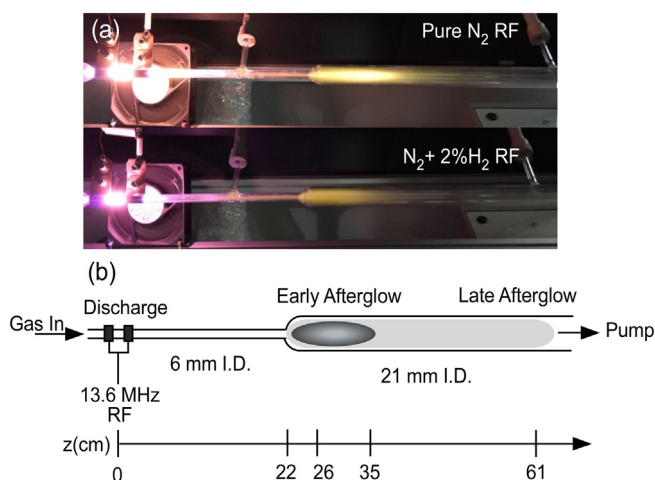


Fig. 1. (a) Pictures of our experimental setup for the generation of RF plasmas of N_2 and $N_2 + H_2$ as well as their afterglows under operating conditions and (b) a schematic diagram of our setup. The position of the measurement along the tube (z) is labelled with respect to the starting point ($z = 0$) of the RF plasma generation.

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